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PLEASE DO NOT RETURN YOUR FORM TO THE ABOVE ADDRESS. 3. DATES COVERED (From - To) 1. REPORT DATE (DD-MM-YYYY) 2. REPORT TYPE 1 December 1999 - 31 January 2004 31 January 2004 FINAL. 5a. CONTRACT NUMBER 4. TITLE AND SUBTITLE 5b. GRANT NUMBER Studies in Buffered Chloroaluminate Ionic Liquids F40620-00-1-0061 **5c. PROGRAM ELEMENT NUMBER** 6. AUTHOR(S) 5d. PROJECT NUMBER 5e. TASK NUMBER Osteryoung, Robert A. 5f. WORK UNIT NUMBER 8. PERFORMING ORGANIZATION 7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) REPORT NUMBER Department of Chemistry North Carolina State University Box 8204 Raleigh, NC 227695-8204 10. SPONSOR/MONITOR'S ACRONYM(S) 9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) **AFOSR** Air Force Office of Scientific Research/NL 4015 Wilson Blvd., Rm. 713 11. SPONSOR/MONITOR'S REPORT Arlington, VA 22203-1954 NUMBER(S) 12. DISTRIBUTION/AVAILABILITY STATEMENT Distribution Unlimited DISTRIBUTION STATEMENTA Approved for Public Release

Distribution Unlimited 20040224 072 13. SUPPLEMENTARY NOTES 14. ABSTRACT Electrochemistry in ambient temperature ionic liquids was performed. A portion of the work was carried out in haloaluminate melts, mainly 1-ethyl-3-ethyl imidazolium chloride - aluminum chloride. This was to complete work initiated under prior grants and involved studies of buffering of these systems. The bulk of the work involved electrochemical studies in non-haloaluminate ionic liquids, mainly 1-butyl-3-methylimidazolium hexafluorophosphate. Alkali metal reduction potentials weree measured, an apparent anomaly with a rotating disc electrode was found and explained, and turn-on potentials and conductivities of polypyrrole films in the non-haloaluminate ionic liquids were measured. 15. SUBJECT TERMS Ionic liquids; rotating disc voltammetry; conducting polymers. 18. NUMBER 19a. NAME OF RESPONSIBLE PERSON 16. SECURITY CLASSIFICATION OF: 17. LIMITATION OF **ABSTRACT** Robert Osteryoung a. REPORT | b. ABSTRACT | c. THIS PAGE PAGES None 19b. TELEPHONE NUMBER (include area code) U U U 9199-515-6970

# Final Report on Grant No.F49620-00-1-0061 Studies in Buffered Chloroaluminate Ionic Liquids

This activity was funded from December 1, 1999 through January 31, 2004 for \$308,423. In addition, a supplement of \$30,545 was added from August 1, 2002 through January 31, 2004. This was added as a separate grant with the same title.

The Principal Investigator has been funded continuously since 1971, by AFOSR. He has been fortunate to have had incredibly capable Program Managers – Denton Elliott, John Wilkes, Hugh De Long, and Paul Trulove – who have allowed him to perform this work. He's also been fortunate to have had superb students and post-docs over the years, without whom none of the work carried out would have been done. Two of his graduate students were Air Force officers sent to do Ph.D. work in the molten salt area. Appendix A lists publications, which acknowledge AFOSR support since support was initiated in 1971. During the period of support, the PI has received several awards, which are listed in Appendix C. All are in part the result of the AFOSR support.

For the past several months, most of the effort has been devoted to winding down all laboratory work and cleaning up a laboratory that has had over 30 years of AFOSR support to amass chemicals and equipment. With the PI's retirement, the laboratory goes to other researchers.

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# SUMMARY OF WORK, 1 December, 1999 - 31 January, 2004

## **Completed Work**

# I. Work Carried Out Under Previous Grant

Several manuscripts listed as "in press" or as "submitted" in the Final Report on Contract F49620-96-1-0097, "Studies of Latent Acidity and Neutral Buffered Chloroaluminate Ionic Liquids," have been published. These include:

Robert A. Osteryoung, "Buffered Chloroaluminate Melts and Latent Acidity," Proceedings of the Twelfth International Symposium on Molten Salts, P.C. Trulove, H. C. De Long, G. R. Stafford, and S. Deki, Eds., Proceedings Volume 99-41, pp. 12-19, The Electrochemical Society, Pennington, NJ (2000).

Diffusion Coefficients of Ferrocene in Composite Materials Containing Ambient Temperature Ionic Liquids, Marek Kosmulski, Robert A. Osteryoung, and Malgorzata Ciszkowska, *J. Electrochem. Soc.*, 147, 1454-1458 (2000).

Use of the Ag/AgCl/Cl Electrode to Estimate Solubility Products in Ambient Temperature Ionic Liquids, Peter Koronaios and Robert A. Osteryoung, J. Electrochem. Soc., 147, 3414-19 (2000).

## II. Work Completed under Present Grant

Most of the work carried out under this present contract has been published, or is in press. Titles and Abstracts of the work follow.

#### A. Haloaluminate Ionic Liquids

Buffering of 1-Ethyl-3-Methylimidazolium Chloride/Aluminum Chloride Melts Using Alkali Metal Bromides and Halides, Peter Koronaios and Robert A. Osteryoung, J. Electrochem. Soc., 148, E483-488 (2001).

Abstract: The buffering of 1-ethyl-3-methyl imidazolium chloride (EMIC) — aluminum trichloride (AlCl<sub>3</sub>) room-temperature ionic liquids (melts) using alkali metal bromides and iodides was studied. The bromide or iodide salts buffer the melts, but the bromide or iodide ions do not replace the chloride ions in the melts. Unlike melts buffered with alkali metal chlorides, it is relatively easy to deposit the alkali metals, and thus it may be possible to use these buffered melts in power sources. In melts buffered with a mixture of lithium chloride and iodide, it is possible to both deposit and strip lithium metal. As has been seen with melts buffered with alkali metal chlorides, the buffered melts appear to be more acidic than would be expected from the low concentration of the acidic Al<sub>2</sub>Cl<sub>7</sub> ion.

Robert A. Mantz, Hugh C. De Long, Robert A. Osteryoung, and Paul C. Trulove, "Studies of Cation Transport in Molten Salts and Molten Salt-Polymer Gels by Pulse-Field Gradient Spin-Echo NMR," Proceedings of the Twelfth International Symposium on Molten Salts, P.C. Trulove, H. C. De Long, G. R. Stafford, and S. Deki, Eds., Proceedings Volume 99-41, pp. 169-176, The Electrochemical Society, Pennington, NJ (2000).

<u>Abstract</u>: Pulsed-field-gradient spin-echo NMR has been used to determine the diffusion coefficients of the cation species in a series of chloroaluminate room-temperature molten salts as well as that of 1,2-dimethyl-3-propylimidzolium tetrafluroborate and a molten salt polymer gel. Based on the diffusion coefficients, the activation energy for diffusion of the melt cations has been calculated. In addition, the hydrodynamic radius of the melt cation has been determined using the Stokes-Einstein relation.

#### B. Studies in Non-Haloaluminate Ionic Liquids

Electrochemical Properties of Alkali Metals in 1-Butyl-3-Methylimidazolium Hexafluorophosphates, Deborah L. Boxall and Robert A. Osteryoung, J. Electrochem. Soc., 149, E185-188 (2002).

Abstract: Formal potentials and diffusion coefficients of the alkali metal couples of lithium, sodium and potassium hexafluorophosphate salts dissolved in 1-butyl-3-methyl-imidazolium hexafluorophosphate were determined using a hanging mercury drop electrode as the working electrode. Chronoamperometry was used to determine the diffusion coefficients, which ranged from  $1.4 \times 10^{-8}$  to  $4.5 \times 10^{-8}$  cm<sup>2</sup>/s for the Na and K cations, respectively. Formal reduction potentials of  $-2.96 \pm 0.006$  V and  $-3.35 \pm 0.003$  V vs. the ferrocene/ferrocenium couple were obtained for sodium and potassium using normal pulse voltammetry. The presence of adsorption maxima in the lithium normal pulse voltammograms necessitated the use of chronopotentiometry to determine a lithium formal potential of  $-2.45 \pm 0.025$  V.

Apparent Anomaly During Rotating Disk Voltammetry in Ionic Liquids, Deborah L. Boxall, John J. O'Dea, and Robert A. Osteryoung, *J. Electrochem. Soc.*, **149**, E468-E471 (2002).

Abstract: An apparent anomaly is described in which maxima on rotating disk voltammograms for ferrocene oxidation in an ionic liquid were found. The ionic liquid, 1-butyl-3-methyl imidazolium hexafluorophosphate, bmimPF<sub>6</sub>, is a neoteric solvent of current interest. The maxima are shown to be due to the very high viscosity of the solvent, 3.26 poise, which yields an unusually high Schmidt number of  $3.5 \times 10^7$ , compared to a value of about  $10^3$  for aqueous solutions. It is estimated that over 100 revolutions of the disk are needed to achieve the Levich

limiting current following application of a voltage step to the disk. The current transient resulting from application of a voltage step to the rotating disk is found to be in agreement with previously developed theory, even for these highly viscous systems. Analysis of the transient permits a determination of the Schmidt numbers without measurement of the viscosity and density of the solvent, or diffusion coefficient of the reacting species.

Switching potentials and conductivity of polypyrrole films prepared in the ionic liquid 1-butyl-3-methylimidazolium hexafluorophosphate, Deborah L. Boxall and Robert A. Osteryoung, *J. Electrochem. Soc.*, **151**, E41-45 (2004).

Abstract: Polypyrrole (ppy) and poly(N-methylpyrrole) (pmpy) films were prepared galvanostatically at the ring of a rotating ring-disk electrode from the corresponding monomers dissolved in the ionic liquid 1-butyl-3methylimidazolium hexafluorophosphate (bmimPF<sub>6</sub>). Rotating ring-disk voltammetry was used to determine switching potentials and conductivity of the films while immersed in bmimPF<sub>6</sub>. Switching potentials of  $0.63 \pm 0.04$  V and  $1.07 \pm 0.03$  V vs. the cobaltocenium/cobaltocene couple,  $[CoCp_2]^{+/0}$ , were determined for the ppy and pmpy films, respectively, from negative potential scan voltammograms. Positive potential scan voltammetry was used to obtain the potential dependent conductivity of the films as the films switched from their insulating (at potentials more negative than switching potential) to quasi-metallic state. Two different computational models (non-linear vs. linear conductance gradients) and two different redox probes ([CoCp<sub>2</sub>]<sup>+/0</sup> and decamethylferrocenium/decamethylferrocene) were used in the calculation of film conductivity. The conductivity of the ppy films was found to increase by an order of magnitude for every  $72 \pm 8$  mV change in the applied potential. At potentials less than the switching potential, the conductivity of the pmpy films increased ten-fold for every  $110 \pm 15$  mV change in the applied potential. At potentials greater than the switching potential, the pmpy films required a 200 mV change to induce the same degree of change in film conductivity.

#### III. Personnel

#### Senior Research Personnel

Dr. Deborah Boxall

Dr. John O'Dea

Dr. Peter Koranaios

#### APPENDIX A

Publications--Grant Related Activity - since AFOSR support initiated.

## AFOSR-71-1955; 1 Jan. 1971 - 28 Feb. 1975

- Janet Osteryoung and R. A. Osteryoung, "The Advantage of Charge Measurements for Determining Kinetic Parameters," Electrochimica Acta, <u>16</u>, 525 (1971).
- 2. R. A. Osteryoung, "Introduction to the On-Line Use of Computers in Electrochemistry," Vol. II, "Application of Computers to Chemical Instrumentation," Ed. by Mattson, Mark and MacDonald, Marcel Dekker (1973).
- 3. L. G. Boxall, H. L. Jones and R. A. Osteryoung, "Solvent Equilibria in AlCl<sub>3</sub>-NaCl Melts," J. Electrochem. Soc., <u>120(2)</u>, 223 (1973).
- 4. H. Lloyd Jones, L. G. Boxall and R. A. Osteryoung, "Organic Electrode Reactions in Fused AlCl<sub>3</sub> Containing Solvents," J. Electroanal. Chem., <u>38</u>, 476 (1972).
- 5. L. G. Boxall, H. L. Jones and R. A. Osteryoung, "Electrochemical Studies on Ag, Fe and Cu Species in AlCl<sub>3</sub>-NaCl Melts," J. Electroanal. Chem., <u>121</u>, 212 (1974).
- 6. H. Lloyd Jones and R. A. Osteryoung, "Electrode Reactions of Aromatic Amines in Solvents Containing Fused AlCl<sub>3</sub>: II.," J. Electroanal. Chem., <u>49</u>, 281 (1974).
- 7. R. J. Gale and R. A. Osteryoung, "Investigation of Subvalent Ion Effects During Aluminum Anodization in Molten NaCl-AlCl<sub>3</sub> Solvents," J. Electrochem. Soc., 121, 983 (1974).
- 8. V. R. Koch, L. L. Miller and R. A. Osteryoung, "Reductive Defunctionalization of 1-substituted Adamantanes in Molten Sodium Tetrachloroaluminate," J. Org. Chem., 39, 2416 (1974).
- 9. H. Lloyd Jones and R. A. Osteryoung, "Organic Reactions in Molten Tetrachloroaluminate Solvents," Advances in Molten Salt Chemistry, Vol. 3, Edited by J. Braunstein, G. P. Smith and G. Mamantov, Plenum Publishing (1975).
- 10. R. J. Gale and R. A. Osteryoung, "Dissociative Chlorination of Nitrogen Oxides and Oxyanions in Molten Sodium Chloride-Aluminum Chloride Solvent," Inorg. Chem., 14, 1232 (1975).
- 11. H. L. Chum, V. R. Koch, L. L. Miller and R. A. Osteryoung, "An

- Electrochemical Scrutiny of Organometallic Iron Complexes and Hexamethylbenzene in a Room Temperature Molten Salt," J. Am. Chem. Soc., 97, 3264 (1975).
- 12. D.E. Bartak and R. A. Osteryoung, "The Electrochemical Oxidation of N,N,N',N'-Tetramethylbenzidine in Molten Sodium Tetrachloroaluminate," J. Electrochem. Soc., 122, 600 (1975).
- 13. J. Phillips, R. J. Gale, R. G. Wier and R. A. Osteryoung, "Glassy Carbon Rotating Ring-Disc Electrodes for Molten Salt Studies," Anal Chem., 48, 1266 (1976).
- 14. D. E. Bartak and R. A. Osteryoung, "The Redox Behavior of Tetrachloro-p-Benzoquinone-Tetrachlorohydroquinone Systems in Molten Aluminum Chloride-Sodium Chloride Solvents," J. Electroanal. Chem., 74, 69 (1976).

#### AFOSR 75-2776; 1 March 1975 - 31 May 1976

- 15. V. R. Koch, L. L. Miller and R. A. Osteryoung, "Electroinitiated Friedel-Crafts Transalkylations in a Room Temperature Molten Salt Media," J. Am. Chem. Soc., 98, 5377 (1976).
- 16. K. A. Paulsen and R. A. Osteryoung, "Electrochemical Studies on Sulfur and Sulfides in AlCl<sub>3</sub>-NaCl Melts," J. Am. Chem. Soc., <u>98</u>, 6866 (1976).
- 17. R. A. Osteryoung, "Chemistry and Electrochemistry in Aluminum Chloride Molten Salt Systems," Proceedings of the Symposium on Molten Salts, edited by J. P. Pemsler, J. Braunstein, K. Nobe, D. R. Morris, pp. 240-253, The Electrochemical Society, Pennington, NJ (1976).

#### AFOSR 766-2978; 1 April 1976 - 30 June, 1979

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- J. Robinson, B. Gilbert and R. A. Osteryoung, "The Acid-Base Chemistry of Oxide and Chalcogenides in Sodium Tetrachloroaluminate Melts at 175°C," Inorg. Chem., 16, 3040 (1977).
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- 21. Helena Li Chum, D. Koran and R. A. Osteryoung, "The Electrochemical Behavior of Metal Carbonyls in a Mixture of a Room Temperature Molten Salt and Benzene," J. Organometallic Chem., 140, 349 (1977).

- 22. Helena Li Chum, D. Koran and R. A. Osteryoung, "Photochemistry of Iron(II)Diimine Complexes in a Room Temperature Molten Salt," J. Am. Chem. Soc., 100, 310 (1978).
- 23. J. Robinson and R. A. Osteryoung, "Electrochemical Studies of Selenium and Selenium Compounds in Molten Sodium Tetrachloroaluminate Melts," J. Electrochem. Soc., 125, 1454 (1978).
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- 27. J. Robinson and R. A. Osteryoung, "The Electrochemical Behavior of Te(IV) in Sodium Tetrachloroaluminates," J. Electrochem. Soc., <u>125</u>, 1784 (1978).
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- J. Robinson, R. C. Bugle, H. L. Chum, D. Koran and R. A. Osteryoung, <sup>1</sup>H and <sup>13</sup>C Nuclear Magnetic Resonance Spectroscopy Studies of Aluminum Halide-Alkyl Pyridinium Halide Molten Salts and Their Benzene Solutions," J. Am. Chem. Soc, <u>101</u>, 3776 (1979).
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# AFOSR F49620-79-C-0142: 1 June 1979 - 30 Sept. 1980

- J. Robinson and R. A. Osteryoung, "The Electrochemical Behavior of Aluminum in the Low Temperature Molten Salt System n-Butyl Pyridinium Chloride; Aluminum Chloride and Mixtures of this Molten Salt with Benzene," J. Electrochem. Soc., 127, 122 (1980).
- 32. J. Robinson and R. A. Osteryoung, "An Investigation into the Electrochemical Oxidation of Some Aromatic Amines in the Room Temperature Molten Salt

- System AlCl<sub>3</sub>:N-Butylpyridinium Chloride," J. Am. Chem. Soc., <u>102</u>, 4415 (1980).
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- 37. Koichi Aoki, R. A. Osteryoung and Janet Osteryoung, "Differential Normal Pulse Voltammetry," J. Electroanal. Chem., 110, 1-18 (1980).

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- \*42. T. R. Brumleve, John J. O'Dea, Robert Osteryoung and Janet Osteryoung, "Differential Normal Pulse Voltammetry in the Alternate Pulse Mode Reversible Electrode Reactions," Anal. Chem., <u>53</u>, 702 (1981).
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- 47. C. Nanjundiah, K. Shimizu and R. A. Osteryoung, "Electrochemical Studies of Fe(II) and Fe(III) in an Aluminum Chloride-Butylpyridinium Chloride Ionic Liquid," J. Electrochem. Soc., <u>129</u>, 2474 (1982).
- 48. G. T. Cheek and R. A. Osteryoung, "Preparation and Characterization of a Substituted Alkylpyridinium Chloroaluminate Molten Salt System," Inorg. Chem., 21, 3581 (1982).
- 49. G. T. Cheek and R. A. Osteryoung, "An Electrochemical and Infra-red Study of Chloranil in n-Butylpyridinium Chloride: Aluminum Chloride Ionic Liquid," J. Electrochem. Soc., 129, 2739 (1982).
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- 59. G. T. Cheek and R. A. Osteryoung, "Preparation and Characterization of a Substituted Alkylpyridinium Chloroaluminate Molten Salt System," Inorg. Chem., 21, 3581 (1982).
- M. Lipsztajn and R. A. Osteryoung, "Increased Electrochemical Window in Ambient Temperature Ionic Ionic Liquids," J. Electrochem. Soc., <u>130</u>, 1968 (1983).
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- 63. P. G. Pickup and R. A. Osteryoung, "Polymer Coated Electrodes in Ambient Temperature Ionic Liquids," J. Electrochem. Soc., <u>130</u>, 1965 (1983).
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- 65. P. G. Pickup and R. A. Osteryoung, "Electrochemical Polymerization of Pyrrole and Electrochemistry of Polypyrrole Films in Ambient Temperature Molten Salts," J. Am. Chem. Soc., <u>106</u>, 2294 (1984).

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- 67. P. G. Pickup and Robert A. Osteryoung, Charge Transport in Poly-[Ru(2,2'-Bipyridine) (4-Vinylpyridine)]<sup>3+/2+</sup> Films in AlCl<sub>3</sub> /N-(1-Butyl)pyridinium Chloride and AlCl<sub>3</sub> /1-Methyl(3-Ethyl)imidazolium Chloride Molten Salts" J. Electroanal. Chem., <u>186</u>, 99 (1985).
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#### APPENDIX B

Presentations at Meetings Related to Activities on Grant No.F49620-00-1-0061 Studies in Buffered Chloroaluminate Ionic Liquids December 1, 1999 through January 31, 2004

#### **Invited Presentations**

Robert A. Osteryoung, "Ambient Temperature Chloroaluminate Ionic Liquids: An Overview," Keynote Address, International Society of Electrochemistry, Warsaw, Poland, September 2000.

Robert A. Osteryoung, "An Overview of Chloroaluminate Ionic Liquids," Foster Chemistry Colloquium Speaker, SUNY-Buffalo, October 27, 2001.

Deborah L. Boxall and R. A. Osteryoung, "Electrochemical Investigations in the Ionic Liquid 1-Butyl-3-Methylimidazolium Hexafluorophosphate," 13th International Symposium on Molten Salts, The Electrochemical Society, Philadelphia, PA, May, 2002.

#### **Contributed Presentations**

D.L Boxall, J.J. O'Dea and R.A. Osteryoung, "Determination of Conductive Polymer Switching Potentials by Rotating Ring-Disk Voltammetry," Southeast Regional Meeting of the American Chemical Society, October 2002, Charleston.

#### APPENDIX C

# Honors and Awards to PI during period of AFOSR support.

- Distinguished Service Award, Colorado State University, 1975.
- American Chemical Society Colorado Section Award, 1978.
- Elected Fellow, American Association for the Advancement of Science, 1980.
- Winner of C. N. Reilley Award in Electroanalytical Chemistry, 1987
- Awarded Schoellkopf Medal, Western New York Section, American Chemical Society 1990
- Elected as Fellow, The Electrochemical Society, 1990-
- Recipient of the American Chemical Society, Division of Analytical Chemistry, Award in Electrochemistry1991.
- Recipient of the Physical Electrochemistry Division of the Electrochemical Society Max Bredig Award in Molten Salt Chemistry, 1991
- -Outstanding Alumnus of the Year Award, College of Arts and Sciences, Ohio University, 1992